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INTRODUCTION

Recently there has been considerable interest in designing shaped laser pulses to control molecular systems (1-4). One objective has been to perform molecular site-selective chemistry. In order to achieve such ambitious goals, many uncertainties and complications have to be overcome. The Molecular Dynamics Simulator (MDS) is a tool that has been developed to help gain insight into the physical issues and problems that may arise when dynamics of real molecules are controlled in a laboratory environment. The use of a physical simulator is especially useful since it focuses attention on the validity of approximations for describing the true system, and it also forces one to consider real laboratory noise and imprecision. The MDS is a bench top electro-mechanical simulator of driven molecular dynamical motion and includes the capability of simulating chemical bond breaking. Since the MDS operates on the comfortable time scale of seconds and its actions are directly visible, it is possible to identify easily and often intuitively both favorable and undesirable behavior. The MDS is an inexpensive forerunner to true laser control experiments, and it provides an ongoing testing ground for new concepts in molecular manipulation and control prior to their full implementation. The MDS reported here is a significant extension of an earlier version (5-6) in that the simulated molecular bonds are now non-linear.

The MDS operates naturally as a classical mechanical device, and so it is necessary to consider the significance of classical mechanics when modeling molecular interactions. Although quantum mechanics provides the proper description for designing optimal controllers of molecular systems, the calculations are currently impractical for systems of more than three or four degrees of freedom. Furthermore, in many cases classical mechanics may be used as an approximate description of the average quantum mechanical

dynamics. This is a good approximation for cases in which the system size is much greater than the de Broglie wavelength and when wave packet spreading and tunneling are avoided or are insignificant. In these cases, computer simulations indicate that classical descriptions may often be quite adequate (7).

MDS DESCRIPTION AND THE SIMULATED INTERATOMIC POTENTIAL

The MDS consists of carts, representing atoms, which float on a nearly frictionless linear air track and a mechanical driver which is the analog of a laser (Fig. 1). The positions of the carts and the driver are traced using optical position detectors connected to a computer. The position sensing method requires that battery operated LEDs be placed on the carts and driver, and linear photodetectors be located alongside them. The driver detector is used with a proportional integral (PI) feedback circuit to remove mechanical loading effects due to the inertia of the carts, in addition to providing driver position information. Each cart provides a vibrational degree of freedom for the model of a molecule, and the driver represents the forcing by a laser. This MDS evolved out of an earlier version in which mechanical springs, both harmonic and nonlinear were used to join the carts and driver. We found however, that the configuration of small rare earth magnets in Fig. 2 provides a much more realistic representation of a molecular potential. The cart/driver schematic in Fig. 2 shows the stable equilibrium distance corresponding to the bottom of the potential well at 0.7cm. For displacements of the cart to larger relative distances the attractions between the nearest poles of the three dipoles dominates so that the net force is attractive. The same concepts apply at the unstable equilibrium point at -0.7cm except that the forces are repulsive since the nearest three poles of the dipoles are the same. By treating the magnets as point dipoles, the following analytic form for the potential was obtained:

$$V(q - \varepsilon) = V_\bullet - \frac{V_1 \times (q - \varepsilon - q_0)}{(x^2 + (q - \varepsilon - q_0)^2)^{5/2}} \qquad (1)$$

A plot of this potential is shown above the cart and driver in Fig. 2 by the solid and dashed lines. Here V_0 and q_0 are arbitrary constants used to define the positions of the axes, V_1 and x are parameters that depend on the strength of the magnets and their relative positions, q is the displacement of the cart in the lab frame, and ε is the driver displacement which is generally much smaller than q. The motion of the cart is restricted to the potential well on the right side of Fig. 2, and the lower part of the steep repulsive wall to the left. The motion of the simulator never entered the unphysical dashed region which differs from models of the true molecular potential which have a steep wall shown by the dotted line. Dissociation occurs when the cart has sufficient energy to escape from the well to the right. The potential is linear in bond displacement $(q-\varepsilon)$ near the inflection point on the repulsive wall, and the soft attractive barrier falls off as $1/(q-\varepsilon)^4$ at large displacements. The potential can also be described by its Taylor expansion in the driver displacement:

$$V = V_{\varepsilon=0} + \left.\frac{\partial V}{\partial \varepsilon}\right|_{\varepsilon=0} \varepsilon + \left.\frac{\partial^2 V}{\partial \varepsilon^2}\right|_{\varepsilon=0} \varepsilon^2 + \ldots \qquad (2)$$

where the second term on the right represents the linear dipole interaction, and the third term the polarizability interaction. In the present form of the MDS it was found that the polarizability term is typically 10% of the linear term. When the MDS is configured with a single cart and driver it simulates the oscillations in a diatomic molecule, and when configured with two carts and a driver it simulates oscillations in a triatomic molecule.

As with the control of a molecular system, it is necessary first to establish the potential. This was done by iteratively performing a series of trial dynamics experiments to be modeled by an appropriate potential. First a test driver function was generated using optimal control theory and approximate values for the potential parameters. Then accurate values of these potential parameters were obtained by fitting the resulting dynamics to the model and the form of the potential was verified as adequate. Fig. 3 shows the response to the driving field, and a fit to it using the equations of motion with the potential form given above.

OPTIMAL CONTROL

In general for small displacements the Hamiltonian of a molecule and also its simulated form is given by

$$H = \frac{1}{2}p^T G p + V(q, \varepsilon) \tag{3}$$

where q and p are vectors containing the positions and momenta of the carts respectively, and G is the Wilson G matrix (8). In the case where only one cart was used p and q become scalars and G becomes the inverse of the mass m. The equations of motion are given by Hamilton's equations

$$\dot{q} = \frac{\partial H}{\partial p} = \frac{p(t)}{m} \tag{4}$$

$$\dot{p} = -\frac{\partial H}{\partial q} = -\frac{\partial V}{\partial q} - \alpha p(t) \tag{5}$$

where αp is added as the damping term of the cart motion and is assumed to be proportional to velocity. In matrix form these equations are represented by

$$\dot{z} = f(z,t) \quad \text{where} \quad z(t) = \begin{pmatrix} q(t) \\ p(t) \end{pmatrix} \tag{6}$$

Optimal control theory is used to design a driving function $\varepsilon(t)$ which forces the cart to reach an objective state vector $z(T)$ at the target time T. The driver $\varepsilon(t)$ cannot be an arbitrary function for a real laser pulse or for the mechanical driver and is subject to various constraints; first it must be a smooth continuous function without any jumps that could not be followed by the driver or laser and secondly the amplitude of the driver at the initial and final times, $\varepsilon(0)$ and $\varepsilon(T)$, must equal zero. The second requirement follows from the first constraint and the fact that before and after the time interval the driving field has zero amplitude. These constraints are met by representing $\varepsilon(t)$ by a Fourier series of sine functions:

$$\varepsilon(t) = \sum_{i=1}^{N} C_i \sin\left(\frac{i\pi t}{T}\right) \tag{7}$$

By keeping N small one can restrict the form of the solution, and avoid unwanted high frequency behavior.

Optimal control theory uses a cost functional which is minimized by adjusting $\varepsilon(t)$, and eventually calculates an optimum driving field $\varepsilon(t)$ to reach the objective subject to the constraints. The cost functional used here is given by

$$J = \frac{1}{2}(z(T) - \gamma)^T P_f (z(T) - \gamma)$$

$$+ \frac{1}{2}\int_0^T dt\left[W_b h\left(q^2 - \frac{\gamma^2 t}{T}\right)\right] \qquad (8)$$

$$+ \frac{1}{2}\int_0^T dt\left[z(t)^T W z(t) + W_e \varepsilon(t)^2\right]$$

where the first term is the deviation from the final objective, γ, weighted with the matrix P_f. The second term is a weighted envelope that restricts the amplitude of the response (bond stretch in this case) below a straight line joining the initial and final states using a smoothed step function $h(s) = \tan^{-1}(gs) + \pi/2$. This function $h(s)$ approaches zero for $s \ll 0$, and π for $s \gg 0$, and its slope is governed by the parameter g. The second term is important since it prevents large oscillations, which accentuate effects due to noise, from occurring near the beginning period. The third term permits the integrated amplitude of the cart and driver to be weighted with W and W_e respectively, and so weights against large amplitude oscillations of the cart and driver over the whole interval encouraging smaller, more controllable dynamics. The same considerations are expected to be of importance in actual controlled molecular dynamics.

To minimize J with the constraint that the equations of motion be satisfied, a Lagrange multiplier vector $\lambda(t)$ is introduced

$$\bar{J} = J - \int_0^T dt\lambda^T(t)[\dot{z} - f(z,\varepsilon)] \qquad (9)$$

and the new cost functional $\bar{J}$ is minimized with respect to λ, z and ε. The resultant optimizing equations were solved numerically, and an optimal

trajectory was generated with the design of ε(t) to be implemented in the MDS. Its action on the simulated molecule was then observed. Despite the presence of laboratory noise and uncertainties in the potential, no special care was taken to include robustness in the design process, but the results proved adequate in this case. Two examples are considered below corresponding to control of di- and triatomic molecules.

RESULTS

In the examples shown here, emphasis is given to issues and observations that have important analogs at the molecular scale. First Fig. 4 shows an optimally designed molecular bond length trajectory for a single cart, (i.e.. a diatomic molecule), which reaches an objective amplitude and momentum after 5 seconds, with four actual runs of the MDS. The designed driving field is shown below the cart trajectory as a solid line and the actual laboratory driver as a dotted line. The plot demonstrates the very good repeatability achieved by the cart's response to successive runs of the driving control field as well as a high degree of accuracy in following the predicted trajectory and in reaching the final objective. The trajectory shown here resulted in dissociation after the control field was turned off. To obtain such accurate and repeatable results there were a number of factors that had to be taken into account, many of which may be analogous to actual molecular control issues.

The model for the potential did not accurately describe large amplitude oscillations, reflecting the fact that fits to large oscillations (>3cm) gave significantly different parameters than fits to smaller ones (<1cm). In order to produce accurate predictions for the trajectories, it was necessary to restrict the amplitude of the oscillations to be under 1cm until the final "kick" from the driver caused dissociation as shown in Fig. 4. In true molecular dynamics the

potentials often have to be approximated. Here too, information at higher energies is often less reliable, and so a designed trajectory may have to be restricted in a similar way.

Noise in the initial conditions due to air fluctuations had to be suppressed since it caused a phase shift and significant deviations in the resulting trajectory. Likewise errors in the specification of the initial molecular state could degrade the effectiveness of molecular optimal control. Damping was also a factor, and was adequately modeled as being proportional to the velocity.

One interesting observation was the effect of an extra unmodeled degree of freedom in our apparatus. It was found that as the cart approached the driver a small torque initiated sideways oscillations which modified the linear motion. The net effect here was the introduction of an unmodeled term in the Hamiltonian which caused non repeatable motion and a significant loss in accuracy. The torque could be due to slightly different strength magnets on the cart, misalignment of the driver magnet, or imperfections in the dipole nature of the magnets. The lateral oscillations were greatly reduced by a change in geometry (reducing the moment arm) and by careful alignment of the magnet on the driver with respect to the cart magnets. As a result the repeatability of the cart runs was significantly increased. This overall situation once again has a molecular analogy in that an incomplete model of the molecule one is attempting to control, or incomplete knowledge of the laser-molecular interaction can influence the overall performance of the optimal controller.

In the control of real molecular dynamics, the propagation of the laser pulse through a sample medium can change the laser field. Similarly the mechanical driver is influenced by the cart motions and PI feedback is needed to cause the driver to accurately track a desired trajectory as shown in Fig. 4.

Analogous steps will have to be considered when designing an optimal field for a molecular system.

After successfully controlling the single cart model, an additional cart was added to simulate a triatomic molecule using a magnetic bond similar to the one joining the driver and the first cart. The equations of motion and the cost functional were extended in a straightforward manner to account for the extra degree of freedom, and then the potential of the second bond was found in a similar way to the potential of the first bond but using the new equations of motion. Optimal control theory was then used to generate a theoretical driving field to force the carts to obtain objective displacements at a given time. The responses of the carts to this driving field are shown in Fig. 5, along with the predicted response of the carts. Here the MDS maps onto a family of possible triatomic molecules including the case of the stretched target bond being the stronger of the two. These plots show very good control over almost the full trajectory. Not surprisingly the control of the carts is not quite as precise as the single cart case due to uncertainties in both bond potentials. Thus these results strongly suggest the need for improved control in order to achieve designed bond breaking.

CONCLUSION

The MDS provides a low cost method of testing the viability of different schemes to control molecular dynamics, as well as helping in assessing which factors could be important. The first example presented here of a one degree-of-freedom diatomic molecule, successfully demonstrates controlled dissociation of a bond. The second example shows that control can be extended to molecules with more degrees of freedom. By carrying out this laboratory demonstration, we were forced to deal with many experimental uncertainties that one could

expect to encounter for actual bond selective chemistry. The advantages of the MDS over computer simulations alone includes the necessity to consider many experimental factors that might otherwise have been overlooked in a computer model such as an incomplete knowledge of the potential form or an unmodeled degree of freedom. Given also that the MDS models a non-linear oscillator, it is an excellent apparatus to test the robustness of optimal control theory.

Additional carts could be added to simulate larger polyatomic molecules as was done in the linear harmonic MDS (9). A true simulation of selective chemistry could be tested in which one of the bonds is broken while the other is left intact, and the robustness of the optimal control theory examined. Chaotic behavior may also be observed in systems with a larger number of degrees of freedom, and its possible effects on the achievement of control investigated (10). The MDS may also be suitable for testing other proposed methods of achieving selective chemistry. An example would be the use of closed-loop learning algorithms to circumvent the computer design process on the incompletely known molecular system in which the simulated molecule teaches the driver how to achieve its control (11). Eventually a desired response would be generated without having to provide a detailed model for the potential, and its MDS evaluation could be a valuable forerunner to actual molecular implementation.

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Fig. 1. Diagram of the Molecular Dynamics Simulator (MDS). Carts floating on a near frictionless air track are driven by a computer controlled driver, and their positions are measured by linear photodetectors.
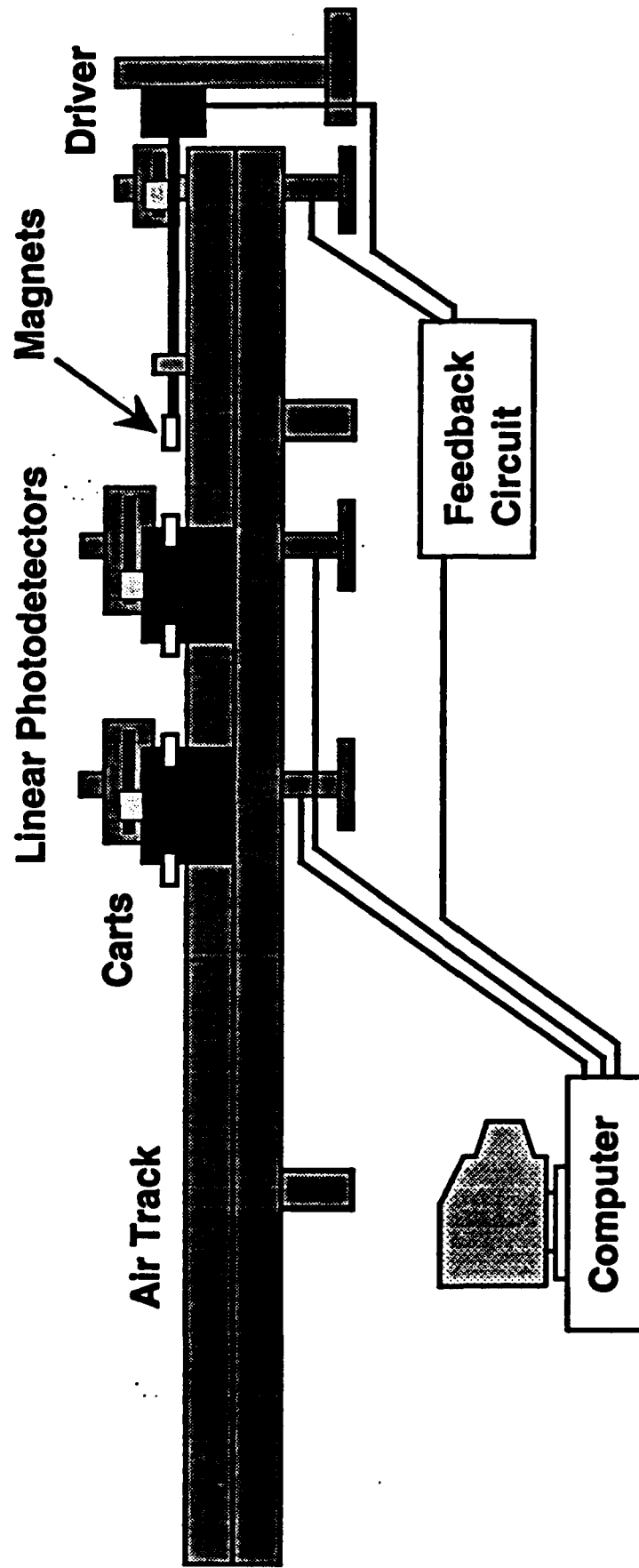
Fig. 2. The potential energy of a magnetically simulated bond is shown against relative distance between the driver and the cart. The solid line covers the region accessed by the dynamics. The dashed line shows the actual potential energy of the magnetic bond. For comparison the dotted line indicates how a realistic molecular bond would appear. The driver and cart are shown in their equilibrium positions below.

Fig. 3. The response of the cart (upper line) to a test driver function (lower line) to determine the parameters of the potential energy curve. The solid line is a three parameter fit using the equations of motion assuming a potential of the form given in equation (1).

Fig. 4. The response of the cart to an optimally generated driving function. The upper solid line is the predicted path for the cart, and the four dotted lines show successive laboratory trajectories of the cart, demonstrating good control and repeatability. The lower solid line is the generated driver function and the dotted line the actual driver path. The cart dissociated after the end of the plot.

Fig. 5. A simulated triatomic molecule. The solid lines show the designed driver function and the predicted trajectories of both carts. The final target is a maximum separation of the two carts with a minimal separation of the driver and first cart. The dashed lines show four consecutive trajectories of the carts.
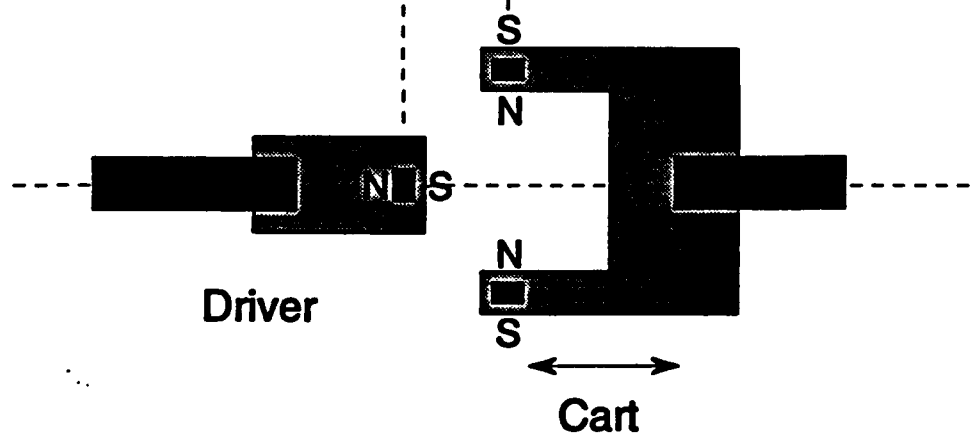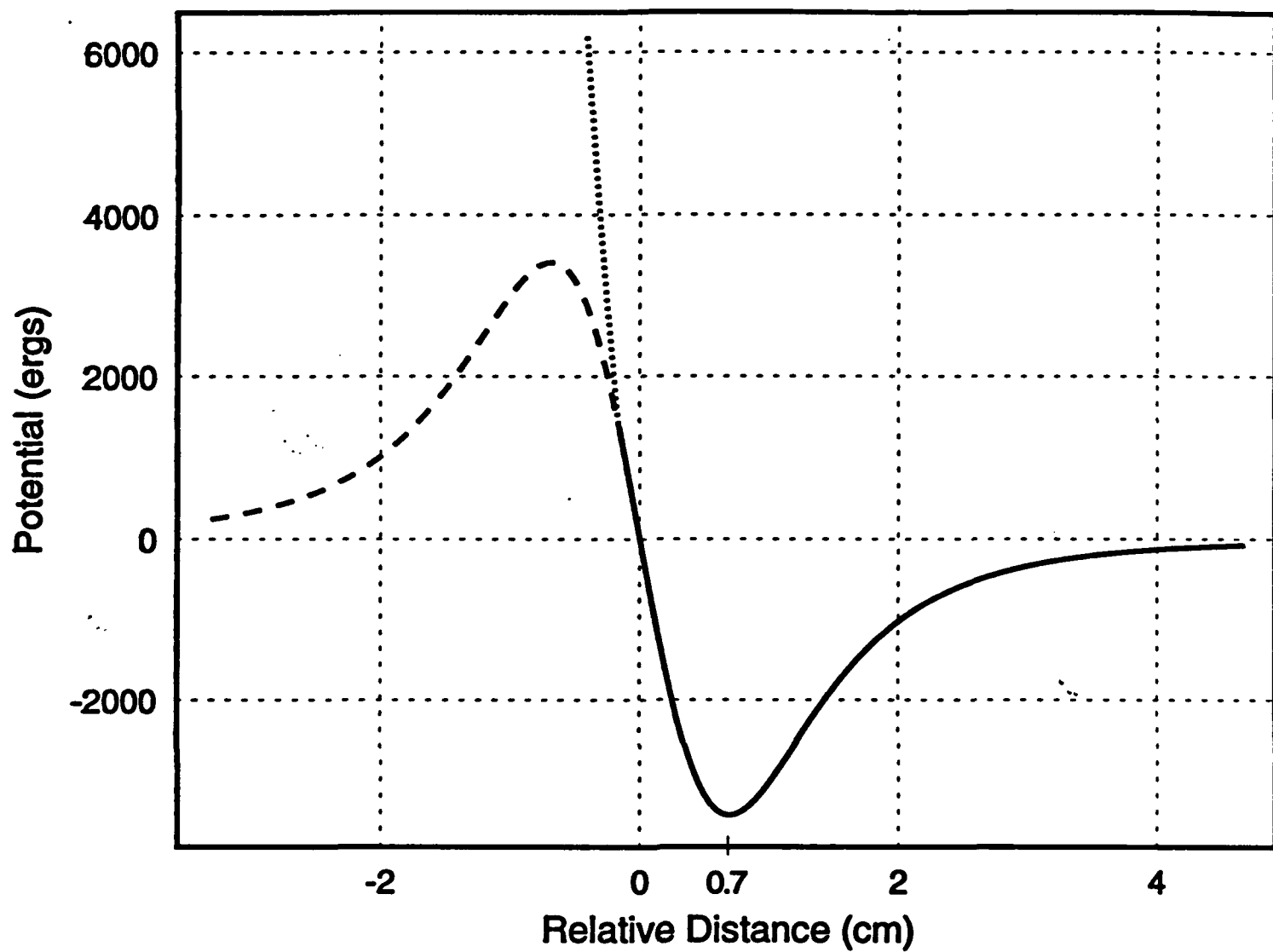
Figure 1

Driver
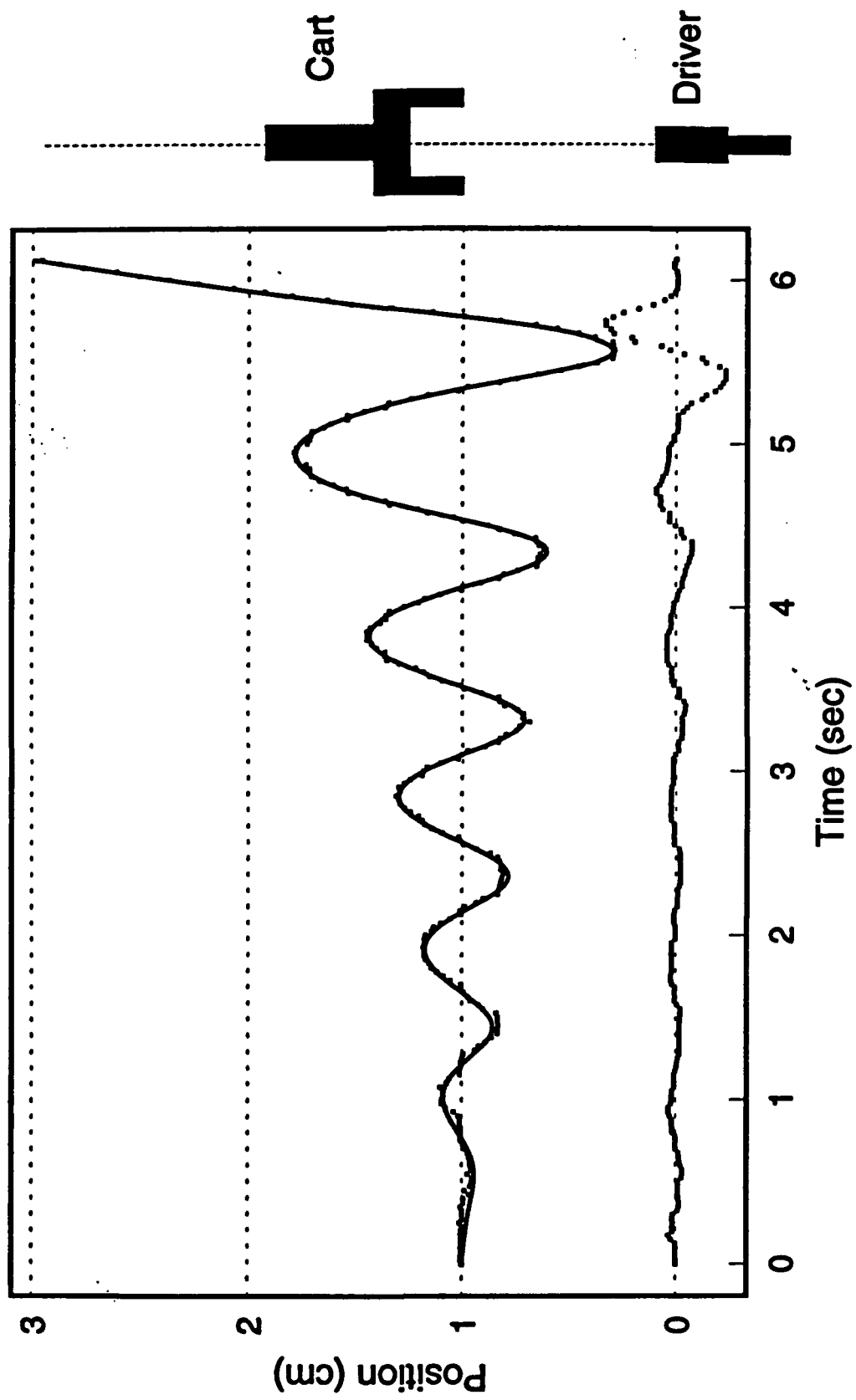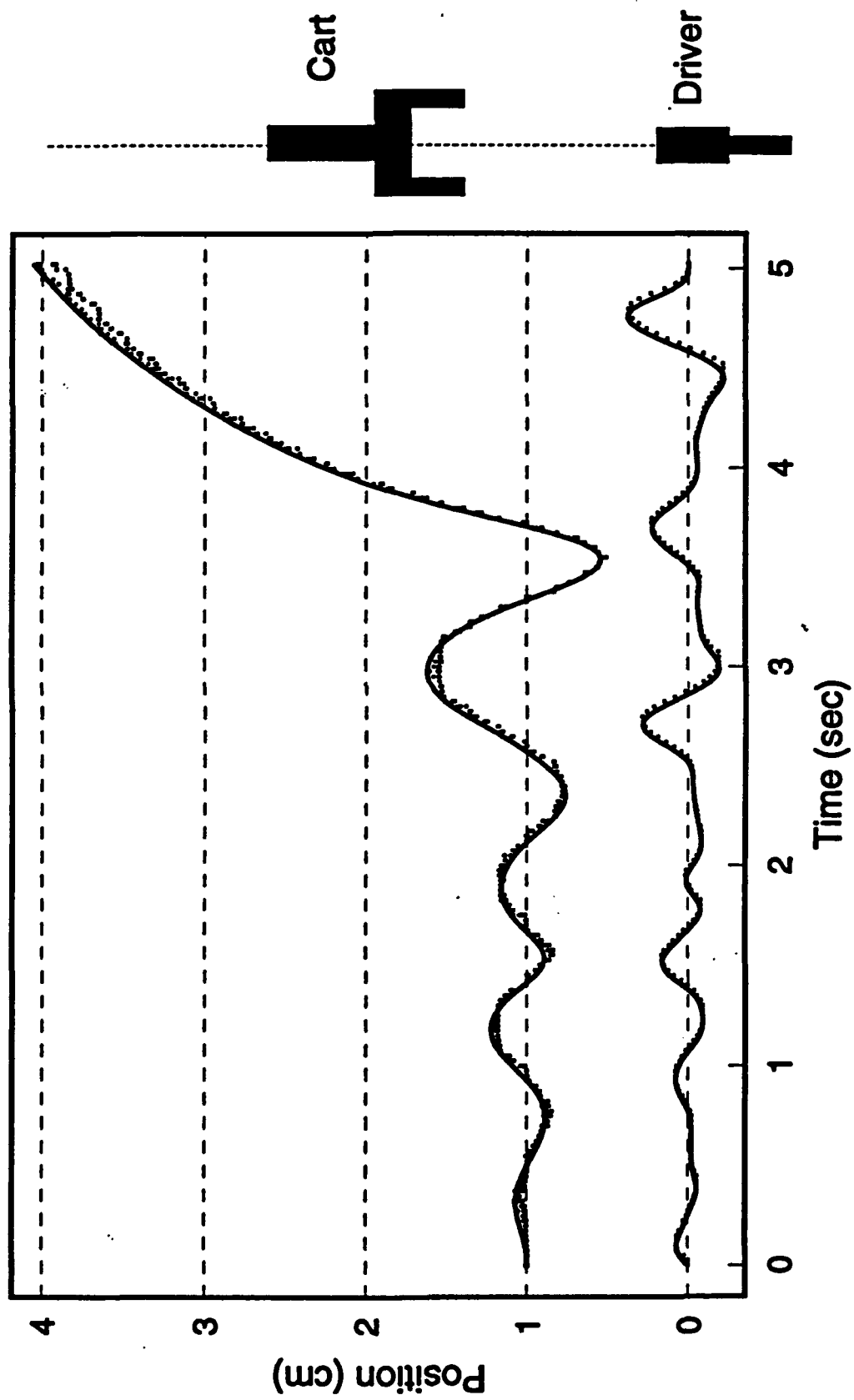
Magnets

Linear Photodetectors

Carts

Air Track

Feedback Circuit

Computer

Figure 2

Figure 3

Figure 4

Cart

Driver

Figure 5